

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF PAPER STRENGTHENING AGENT

(57)Abstract:

PURPOSE: To provide the strengthening agent less apt to be affected by a change in pH by copolymerizing a specific vinylic monomer, a specific vinylic monomer having a carboxyl group, etc., a specific polyvinylic monomer and (meth)acrylamide each in a specific proportion under specific conditions.

CONSTITUTION: Monomers comprising (A) 0.5-20mol.% of a tertiary amino group-having vinylic monomer (salt) and/or its quaternary ammonium salt, (B) 0.5-20mol.% of a vinylic monomer (salt) having a carboxyl group and/or a sulfonyl group, (C) 0.01-2mol.% of a polyvinylic monomer such as methylene bisacrylamide, and (D) 55-98.99mol.% of (meth)acrylamide are copolymerized by a method comprising (i) the components A-D are continuously added dropwise and copolymerized, (ii) the components A, B and C are continuously added dropwise thereto and copolymerized in the presence of the component C, (iii) after the components B and C are copolymerized, the components A and D are continuously added dropwise thereto and copolymerized, or (iv) after the components B and D are copolymerized in the presence of the component C, the components A and D are copolymerized, thus providing the objective paper strengthening agent.

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CLAIMS

[Claim(s)]

[Claim 1] The quarternary ammonium salt (a) obtained by the reaction with the vinyl system monomers which have the 3rd class amino group, those salts, and/or the 4th class-ized agent 0.5 - 20-mol%, The vinyl system monomers which have a carboxyl group and/or a sulfone radical, and those salts (b) 0.5 - 20-mol%, Polyvinyl system monomer (c) 0.01-2-mol %, acrylamide (d) (meta) The manufacture approach of the paper reinforcing agent characterized by carrying out the polymerization of the configuration monomer which consists of 55 - 98.99mol% by the approach of following 1-4.

By carrying out continuation dropping of (a), (b), and the (d) under a polymerization and [2] (c) existence by carrying out continuation dropping of [1 (a)], (b), (c), and the (d), a polymerization, They are a polymerization and [Claim 2] by carrying out continuation dropping of (a) and the (d), after carrying out a polymerization by carrying out continuation dropping of (b) and the (d) under a polymerization and existence of [4 (c)] by carrying out continuation dropping of (a) and the (d) after carrying out the polymerization of [3 (b)], (c), and the (d). The approach given in the 1st term of a patent claim characterized by the time amount which trickles a monomer continuously being total, and being 40 - 120 minutes.

[Claim 3] The approach of [3] and [4] publications of the 1st term of a patent claim characterized by the mole ratios of the division in the second half of first half: being 1:23-1:1 when dividing (d) into the polymerization of the first half, and the polymerization of the second half.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the paper reinforcing agent of paper. Furthermore, in detail, to fluctuation of pH (paper making pH is called hereafter) of the pulp slurry at the time of carrying out paper making of the copolymer manufactured with the polymerization method of this invention, fluctuation of effectiveness is small and the fall of effectiveness offers the approach that a small paper reinforcing agent can be manufactured, to the mineral salt of the dissolution component which exists in a pulp slurry, for example, a sodium sulfate, a calcium sulfate, etc.

[0002]

[Description of the Prior Art] The former and a paper reinforcing agent have independent use of anionic polyacrylamide (polyacrylamide is hereafter called Pulse Amplitude Modulation) in use. ***** Further improvement in the shift to closed ** or neutral paper making of Hokusui by problems, such as wastewater regulation, poor fixing of the sizing compound accompanying it, filterability, a loading material yield, etc. is made into the purpose. According to concomitant use of anionic Pulse Amplitude Modulation and both sexes (cation) Pulse Amplitude Modulation Filterability ability, the fixing engine performance of a loading material or a sizing compound, the paper durability effectiveness, etc. have improved. Moreover, recently, the simultaneous adding formula of anionic Pulse Amplitude Modulation and both sexes (cation) Pulse Amplitude Modulation and a mixed addition formula are developed, and fixing of the further filterability ability and a sizing compound and the paper durability effectiveness can be expected now. However, in respect of a facility, it is [2 sequence] necessary for the object for anions, and for both sexes (cation). Moreover, it is known that the whiteness degree to which importance is attached in the western paper field will also fall greatly. up to the microfilament to which this reduces a whiteness degree greatly by condensation of anionic Pulse Amplitude Modulation and both sexes (cation) Pulse Amplitude Modulation, the dust in the Hokusui system, etc. -- Kaminaka -- yield **** -- things are a big factor. Furthermore, also when the fall of the formation of paper poses a problem from the strength of cohesive force, it has come out. Recently comes and the paper reinforcing agent manufactured considering the cationic vinyl system monomer and acrylamide of the quarternary ammonium salt obtained by the reaction with the vinyl system monomers which have the 3rd class amino group, those salts, and/or the 4th class-sized agent as a main raw material is beginning to be used considerably. Generally these paper reinforcing agents are used independently, and have an effective paper-making pH field comparatively large as independent use, and paper durability reinforcement, the fixing effectiveness of a sizing compound, the yield effectiveness of a loading material, the description that a whiteness degree fall is small, etc. are acquired. however, compared with the conventional anion Pulse Amplitude Modulation and concomitant use of both sexes (cation) Pulse Amplitude Modulation, it is now in respect of the reinforcement in these independent use -- what is satisfied is not obtained.

[0003]

[Problem(s) to be Solved by the Invention] This invention by changing the manufacture approach

of the paper reinforcing agent manufactured considering the cationic vinyl system monomer and acrylamide of the quarternary ammonium salt obtained by the reaction with the vinyl system monomers which have the conventional 3rd class amino group, those salts, and/or the 4th class-sized agent as a main raw material. The paper durability effectiveness is high, and fluctuation of effectiveness is [as opposed to / further / fluctuation of pH] small, and fluctuation of effectiveness offers a small paper reinforcing agent to the dissolution component which exists in a pulp slurry.

[0004]

[Means for Solving the Problem] The quarternary ammonium salt (a) obtained by the reaction with the vinyl system monomers which have the 3rd class amino group, those salts, and/or the 4th class-sized agent this invention. Namely, 0.5 – 20-mol%, The vinyl system monomers which have a carboxyl group and/or a sulfone radical, and those salts (b) 0.5 – 20-mol%, Polyvinyl system monomer (c) 0.01–2 mol%, acrylamide (meta) (d). It is related with the manufacture approach of the paper reinforcing agent characterized by carrying out the polymerization of the configuration monomer component which consists of 55 – 98.99mol% by the following approach. The manufacture approach of the paper reinforcing agent considered as a polymerization and the mark by carrying out continuation dropping of [1 (a)], (b), (c), and the (d).

By carrying out continuation dropping of (a), (b), and the (d) under [2] (c) existence, a polymerization, It is a polymerization and [0005] by carrying out continuation dropping of (a) and the (d), after carrying out a polymerization by carrying out continuation dropping of (b) and the (d) under a polymerization and existence of [4 (c)] by carrying out continuation dropping of (a) and the (d) after carrying out the polymerization of [3 (b)], (c), and the (d). The quarternary ammonium salt hereafter obtained in this invention which explains this invention to a detail by the reaction of the vinyl system monomer and the 4th class-sized agent which have the 3rd class amino group is for example, dimethylaminopropyl (meta) acrylate, dimethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, diethylamino propyl (meta) acrylamide, etc. With the 4th class-sized agent in this invention, chloromethane, benzyl chloride, a p-chlorobenzyl chloride, p-methylbenzyl chloride, p-nitrobenzyl chloride, etc. are lifted. The vinyl system monomer which has quarternary ammonium salt by the reaction of the vinyl system monomer and the 4th class-sized agent which have this the 3rd class amino group can be offered. These amounts of monomers used are usually 0.5–20-mol%, and are 1–10-mol% preferably. 0. Less than [5mol%], a polymer is hard to be fixed to pulp fiber, and there is un-arranging [that the paper durability effectiveness cannot fully be discovered]. It becomes a loss economically and is inconvenient if 20-mol% is exceeded. The vinyl system monomers which have the carboxyl group used for this invention, and those salts can illustrate unsaturated carboxylic acid and those salts, such as a maleic acid, a fumaric acid, an itaconic acid, an acrylic acid (meta), a crotonic acid, or a citraconic acid. The vinyl system monomers which have a sulfone radical, and those salts can illustrate partial saturation sulfonic acids and those salts, such as a vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound (meta) sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and a 2-acrylamide-2-phenyl propane sulfonic acid. These amounts of monomers used are usually 0.5–20-mol%, and are 1–10-mol% preferably. 0. Less than [5mol%], if there is un-arranging on the problem on fixing to the pulp of a paper durability agent and 20-mol% is exceeded, the balance of the amount of cations in a paper durability agent and the amount of anions will pose a problem, and there is un-arranging [that the paper durability effectiveness cannot fully be discovered].

[0006] With the polyvinyl system monomer of this invention, the monomer which has at least two or more double bonds can be raised into a molecule. Specifically, methylenebis acrylamide, diaryl acrylamide, triacrylformal, diacryloyl imide, ethylene glycol acrylate, ethylene glycol dimethacrylate, propylene glycol diacrylate, 1, 3-butylene-glycol dimethacrylate, 1, 4-butylene-glycol dimethacrylate, glycerol dimethacrylate neopentyl glycol dimethacrylate, trimethylolpropane triacrylate, a divinylbenzene, diallyl phthalate, etc. can be used. Although these amounts used change with classes of polyvinyl system monomer and do not generally have *****, it is usually 0.01–2-mol%, and is 0.01–1-mol% preferably. 0. Less than [0.1mol%], when there is un-arranging [that the paper durability effectiveness cannot fully be discovered] and

two-mol% is exceeded, there is un-arranging [that gelation takes place]. If the acrylamide used by this invention (meta) is marketed in the state of fine particles or a water solution and is used industrially, it is enough.

[0007] If it is furthermore a water-soluble object as a polymerization initiator, there will be especially no limit and it will usually be used, dissolving in a monomer water solution. Specifically, the superphosphate like the bromate like a hydrogen peroxide, the peroxide like a benzoyl peroxide, sodium persulfate, potassium persulfate, the persulfate like ammonium persulfate, sodium bromate, and a potassium bromate, fault boron acid sodium, a fault boron acid potassium, fault boron acid ammonium ***** boron acid chloride, a fault sodium carbonate, potassium percarbonate, fault ammonium-carbonate **** percarbonate, perphosphoric acid sodium, a perphosphoric acid potassium, and perphosphoric acid ammonium etc. is mentioned. In this case, although it can be used even if independent, it can use also as a redox system polymerization agent combining a reducing agent. a reducing agent -- ***** -- for example -- a sulfite -- a hydrogensulfite -- iron -- copper -- cobalt -- etc. -- low -- a degree -- ionization -- a salt -- N -- N -- N -- ' -- N -- ' -- tetramethylethylenediamine -- etc. -- organic -- an amine -- reducing sugars, such as ADOSU and a ketose, etc. can be mentioned further. Moreover, as an azo compound, a - azobis-2,4-dimethylvaleronitrile, and 2 and 2'-azobis-4-amidinopropane hydrochloride, 2, and 2 '4, 4'-azobis-4-cyano BAREIN acid, its salt, etc. can be used. Furthermore, it is also possible to use together two or more sorts of above-mentioned polymerization initiators. Polymerization temperature is 30-90 degrees C in general, and it is desirable to control generation of heat by the polymerization and to make the temperature change small. Moreover, it is better for inert gas like nitrogen gas to permute with making a polymerization perform promptly, although especially limitation does not have an ambient atmosphere in curing units. Although especially limitation does not have the continuation drop time of a monomer, it is 40 - 120 minutes preferably in general at 40 - 180 minutes. There are 2 - 4 hours of polymerization time amount preferably in general in 2 - 20 hours.

[0008] The paper reinforcing agent manufactured by the approach of this invention is used in the process which carries out paper making of the pulp, and brings about a big effect for reinforcing the filtration improvement for improving the water break at the time of paper making, and the mechanical reinforcement of paper etc. Although the paper reinforcing agent manufactured by the approach of this invention can also be independently used at this time, you may use together with a sulfuric-acid band, anionic polyacrylamide, MANNIHHI denaturation polyacrylamide, the Hoffmann denaturation polyacrylamide, etc. The addition of the paper reinforcing agent of this invention is each to the desiccation solid content weight of pulp, although it changes with the class of pulp, the speed of paper making, etc. and there is no ***** generally. It is 0.05 - 1% of range preferably 0.01 to 3%. If an addition location is before forming a humid sheet, it will be good anywhere and will usually be added from a refiner outlet before an inlet. In the paper-making system in which a lot of salts exist, the paper durability effectiveness is demonstrated in broad pH field, and the paper manufactured by the above approaches is specifically excellent in bursting strength, compressive strength, Z-axis reinforcement, etc. Therefore, it becomes possible by applying this invention to manufacture paper with the outstanding paper durability reinforcement. The polymer which constructed the bridge partially when the polymerization was carried out about this reason using a polyvinyl monomer like the divinyl monomer of a small amount or a TORIBI nil monomer, although it was not certain generates, and if a monomer is supplied continuously and carries out a polymerization to this, it will become that a polymerization is easy to be carried out by this polymer that constructed the bridge. Therefore, since a polymer has a particle-motion highly [molecular weight], it is thought that it has become that it cannot be easily influenced by pH or ionic strength of a pulp slurry at the time of this paper reinforcing agent being established to pulp.

[0009]

[Example] Next, although this invention is divided into the example of manufacture, and an application according to an example and is explained concretely, this invention is not necessarily limited to the following examples. Moreover, it has set by the GPC method (ShodexGPC System-11, column KB-80M use), and it is 0.1N-NaNO₃ that it is with weight average molecular

weight. Water solution: It is the thing of the polyethylene-glycol reduced property in formamide =3:7 mixed-liquor lower.

To an example 1 Griffin beaker, 312.72 g (91.94-mol%) 40% acrylamide, 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride, 80% 1.72 g (one-mol%) acrylic-acid and itaconic-acid 7.47g (three-mol%) methylenebis acrylamide 177mg (0.06mol%) is adjusted to pH 4.5 in ammoniacal liquor brewing **28%, It considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted 558.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Blowing nitrogen gas after an appropriate time, it agitated and the temperature up of the internal temperature was carried out to 50 degrees C with the water bath. (A) While starting continuation dropping of a solution, continuation dropping of 50g of ammonium persulfate water solutions and the 50g of the sodium-hydrogensulfite water solutions was carried out, the polymerization was started, and the (A) solution was dropped over 70 minutes. Nonvolatile matter 15.7%, Brookfield viscosity in 25 degrees C when it was fixed 50 degrees C and was made to react for 3 hours The both-sexes polymer water solution of the isoelectric point pH 4.8 in 9, 290 cps, pH4.1, weight average molecular weight 800,000, and turbidity was obtained.

[0010] 312.72 g (91.94-mol%) 40% acrylamide, 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride, 1.72 g (one-mol%) 80% acrylic acid, and the 7.47 g (three-mol%) itaconic acid were adjusted to pH 4.5 in ammoniacal liquor brewing **28% at the example 2 Griffin beaker, and it considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 177mg (0.06mol%) and 558.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 4.8 in 15.5% of nonvolatile matters, the Brookfield viscosity 8 in 25 degrees C, 150 cps, pH4.0, weight average molecular weight 1 million, and turbidity.

The brewing **2.5% sulfuric acid adjusted 40% acrylamide 293.17g (86.19mol%) and 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride to pH 4.5 at the example 3 Griffin beaker, and it considered as the (A) solution. In 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 19.55 g (5.75mol%) 40% acrylamide, 1.72 g (one-mol%) acrylic-acid, 7.47 g (three-mol%) itaconic-acid, and methylenebis acrylamide 177mg (0.06mol%) and 558.06 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 80%. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 5.5 in nonvolatile matter 15.7%, the Brookfield viscosity 8 in 25 degrees C, 730 cps, pH4.7, weight average molecular weight 1,300,000, and turbidity.

[0011] 19.55 g (5.75-mol%) acrylamide, 1.72 g (one-mol%) 80% acrylic acid, 7.47g (three-mol%) of itaconic acids, and 58.63 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 40% at the example 4 Griffin beaker, and it considered as the (A) solution. Moreover, the brewing **2.5% sulfuric acid adjusted 40% acrylamide 293.17g (86.19mol%) and 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride to pH 4.5 at the Griffin beaker, and it considered as the (B) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 177mg (0.06mol%) and 499.43 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Blowing nitrogen gas after an appropriate time, it agitated and the temperature up of the internal temperature was carried out to 50 degrees C with the water bath. (A) While starting continuation dropping of a solution, continuation dropping of 50g of ammonium persulfate water solutions and the 50g of the sodium-hydrogensulfite water solutions was carried out, and the polymerization was started. (A) The solution was dropped over 14 minutes, it set for 10 minutes and the (B) solution was dropped over 56 minutes. It was fixed 50 degrees C, and when it was made to react for 3 hours, the both-sexes polymer water solution of the isoelectric point pH 5.5 in nonvolatile matter 15.7%, the Brookfield viscosity 9 in 25 degrees C, 600 cps, pH4.7, weight average molecular weight 1,300,000, and turbidity was obtained.

[0012] In 4 opening flask equipped with example of comparison 1 agitator, a reflux cooling pipe, a

thermometer, and nitrogen gas installation tubing, 312.72 g (91.94mol%) 40% acrylamide, 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride, It brewing ** Ranked second and caustic alkali of sodium adjusted 80% 1.72 g (one-mol%) acrylic-acid, 7.47 g (three-mol%) itaconic-acid, and methylenebis acrylamide 177mg (0.06mol%) and 625.79 g water to pH 4.2 20%. The internal temperature was covered with the back heat insulating material which carried out the temperature up to 50 degrees C, blowing nitrogen gas after an appropriate time.

Agitating, the ammonium persulfate water solution and 10% sodium-hydrogensulfite water solution were thrown in 10%, and the polymerization was started. When water was thrown in after [of reaction peak attainment] 10 minutes and the polymerization reaction was made to complete, the both-sexes polymer water solution of the isoelectric point pH 4.8 in nonvolatile matter 15.4%, the Brookfield viscosity 7 in 25 degrees C, 850 cps, pH4.3, weight average molecular weight 500,000, and turbidity was obtained.

It is 40% acrylamide to an example 5 Griffin beaker. A sulfuric acid adjusts 320.99 g (91.94mol%), 12.34 g (four-mol%) dimethylaminoethyl methacrylate, and 77 g (one-mol%) and 7.67g (three-mol%) methylenebis acrylamide [of 80% acrylic-acid 1. itaconic acids] 182mg (0.06mol%) to pH 4.5 brewing **20%, It considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted 539.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 4.3 in nonvolatile matter 15.6%, the Brookfield viscosity 8 in 25 degrees C, 430 cps, pH4.1, weight average molecular weight 700,000, and turbidity.

[0013] The sulfuric acid adjusted 320.99 g (91.94-mol%) acrylamide, 12.34 g (four-mol%) dimethylaminoethyl methacrylate, 1.77 g (one-mol%) 80% acrylic acid, and the 7.67 g (three-mol%) itaconic acid to pH 4.5 brewing **20% 40% at the example 6 Griffin beaker, and it considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 182mg (0.06mol%) and 539.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 4.3 in nonvolatile matter 15.5%, the Brookfield viscosity 10 in 25 degrees C, 260 cps, pH 4.1 weight average molecular weight 1 million, and turbidity.

The sulfuric acid adjusted 300.93 g (86.19-mol%) acrylamide and 12.34 g (four-mol%) dimethylaminoethyl methacrylate to pH 4.5 brewing **20% 40% at the example 7 Griffin beaker, and it considered as the (A) solution. In 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 20.06 g (5.75mol%) 40% acrylamide, 1.77 g (one-mol%) acrylic-acid, 7.67 g (three-mol%) itaconic-acid, and methylenebis acrylamide 182mg (0.06mol%) and 539.06 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 80%. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 5.5 in nonvolatile matter 15.6%, the Brookfield viscosity 8 in 25 degrees C, 440 cps, pH4.7, weight average molecular weight 1,200,000, and turbidity.

[0014] 20.06 g (5.75-mol%) acrylamide, 1.77 g (one-mol%) 80% acrylic acid, 7.67g (three-mol%) of itaconic acids, and 60.18 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 40% at the example 8 Griffin beaker, and it considered as the (A) solution. Moreover, it is 40% acrylamide 300.93g (86.19mol%) to the Griffin beaker. It is a brewing **20% sulfuric acid about dimethylaminoethyl methacrylate 12.34g (four-mol%). It adjusted to pH 4.5, and considered as the (B) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 182mg (0.06mol%) and 478.88 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 4, and obtained the both-sexes polymer water solution of the isoelectric point pH 5.8 in nonvolatile matter 15.6%, the Brookfield viscosity 7 in 25 degrees C, 320 cps, pH4.8, weight average molecular weight 1,300,000, and turbidity.

[0015] In 4 opening flask equipped with example of comparison 2 agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 320.99 g (91.94mol%) 40% acrylamide, 12.34 g (four-mol%) dimethylaminoethyl methacrylate, 80% 1.77 g (one-mol%) acrylic-acid, 7.67 g (three-

mol%) itaconic-acid, and methylenebis acrylamide 182mg (0.06mol%) And it brewing ** Ranked second and the sulfuric acid adjusted 606.80 g water to pH 4.2 20%. Others performed the same actuation as the example 1 of a comparison, and obtained nonvolatile matter 15.6%, the Brookfield viscosity 6 in 25 degrees C, 970 cps, and the both-sexes polymer water solution of pH4.3.

concentration 1.0% which is 400ml (it is described as Canadian standard freeness and following C.S.F) of degrees of beating obtained from applications 1-8 and the comparison application 1 - 2 corrugated-paper used paper of pulp slurry -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. pH of the pulp slurry at this time was 6.1 and 5.0, respectively. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, and churning was continued for 1 more minute. The pulp slurry obtained after an appropriate time is used, and it is TAPPI. Paper making was carried out by the square shape sheet machine. With the drum dryer, for 110 degrees C and 3 minutes, the wet sheet which carried out paper making performed desiccation, and obtained the handmade paper of basis-weight 150 g/m2. the above handmade paper -- using -- JIS-P -8112 -- applying correspondingly -- a "burst index" and JIS-P -8126 -- applying correspondingly -- " -- a ratio -- "Z-axis reinforcement" was measured and computed using compressive-strength" and a Kumagaya Riki Kogyo internal bond tester, and the result was shown in Table 1.

[0016] applications 9-16 and the comparison applications 3-4 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 9-16 and the comparison applications 3-4 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 2.

applications 17-24 and the comparison applications 5-6 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na2 SO4 opposite pulp -- 5 or 10% -- adding -- CaSO4 opposite pulp -- 200 ppm It added and agitated for 2 minutes. Na2 SO4 adding -- the electric electric conductivity of a pulp slurry -- 0.15 mS/cm from -- 0.8 mS/cm and 1.3 second/cm It changed. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 17-24 and the comparison applications 5-6 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 3.

[0017] applications 25-32 and the comparison applications 7-8 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na2 SO4 opposite pulp -- 5 or 10% -- adding -- CaSO4 opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 25-32 and the comparison applications 7-8 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 4.

applications 33-40 and the comparison applications 9-10 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 33-40 and the comparison applications 9-10 was completely carried out in the same conditions and identity operation with applications 1-8 and

the comparison applications 1-2, and the result was shown in Table 5.

applications 41-48 and the comparison applications 11-12 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 41-48 and the comparison applications 11-12 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 6.

[0018] applications 49-56 and the comparison applications 13-14 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na₂ SO₄ opposite pulp -- 5 or 10% -- adding -- CaSO₄ opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 49-56 and the comparison applications 13-14 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 7. applications 57-64 and the comparison applications 15-16 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na₂ SO₄ opposite pulp -- 5 or 10% -- adding -- CaSO₄ opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 57-64 and the comparison applications 15-16 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 8.

[0019]

[Effect of the Invention] the both-sexes polymer of the former [polymer / which was manufactured the condition in this invention generic claim as shown in Tables 1-8 / both-sexes] -- a ratio -- bursting strength and a ratio -- it excels in engine performance, such as an improvement operation in paper durability shown by compressive strength and Z-axis reinforcement, and is hard to be influenced by pH fluctuation.

[0020]

[Table 1]

the comparison applications 1-2, and the result was shown in Table 5.

applications 41-48 and the comparison applications 11-12 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 41-48 and the comparison applications 11-12 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 6.

[0018] applications 49-56 and the comparison applications 13-14 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na_2SO_4 opposite pulp -- 5 or 10% -- adding -- CaSO_4 opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 49-56 and the comparison applications 13-14 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 7.

applications 57-64 and the comparison applications 15-16 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na_2SO_4 opposite pulp -- 5 or 10% -- adding -- CaSO_4 opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 57-64 and the comparison applications 15-16 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 8.

[0019]

[Effect of the Invention] the both-sexes polymer of the former [polymer / which was manufactured the condition in this invention generic claim as shown in Tables 1-8 / both-sexes] -- a ratio -- bursting strength and a ratio -- it excels in engine performance, such as an improvement operation in paper durability shown by compressive strength and Z-axis reinforcement, and is hard to be influenced by pH fluctuation.

[0020]

[Table 1]

表. 1

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Yg/cm) |
|---------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 1 | 実施例 1 | 0.25 | 6.1 | — | — | 1.76 | 15.8 | 1.77 |
| 応用例 2 | 実施例 1 | 0.25 | 5.0 | — | — | 1.77 | 15.8 | 1.80 |
| 応用例 3 | 実施例 2 | 0.25 | 6.1 | — | — | 1.77 | 15.9 | 1.81 |
| 応用例 4 | 実施例 2 | 0.25 | 5.0 | — | — | 1.79 | 15.8 | 1.85 |
| 応用例 5 | 実施例 3 | 0.25 | 6.1 | — | — | 1.85 | 16.1 | 1.91 |
| 応用例 6 | 実施例 3 | 0.25 | 5.0 | — | — | 1.84 | 15.9 | 1.93 |
| 応用例 7 | 実施例 4 | 0.25 | 6.1 | — | — | 1.86 | 16.2 | 1.93 |
| 応用例 8 | 実施例 4 | 0.25 | 5.0 | — | — | 1.84 | 16.0 | 1.92 |
| 比較応用例 1 | 比較例 1 | 0.25 | 6.1 | — | — | 1.74 | 15.7 | 1.81 |
| 比較応用例 2 | 比較例 1 | 0.25 | 5.0 | — | — | 1.75 | 15.8 | 1.82 |

[0021]

[Table 2]

表. 2

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 9 | 実施例 1 | 0.50 | 6.1 | — | — | 1.90 | 16.4 | 1.99 |
| 応用例 10 | 実施例 1 | 0.50 | 5.0 | — | — | 1.91 | 16.9 | 2.03 |
| 応用例 11 | 実施例 2 | 0.50 | 6.1 | — | — | 1.91 | 16.8 | 2.03 |
| 応用例 12 | 実施例 2 | 0.50 | 5.0 | — | — | 1.93 | 16.9 | 2.05 |
| 応用例 13 | 実施例 3 | 0.50 | 6.1 | — | — | 2.02 | 17.7 | 2.09 |
| 応用例 14 | 実施例 3 | 0.50 | 5.0 | — | — | 2.00 | 17.6 | 2.09 |
| 応用例 15 | 実施例 4 | 0.50 | 6.1 | — | — | 2.03 | 17.8 | 2.11 |
| 応用例 16 | 実施例 4 | 0.50 | 5.0 | — | — | 2.02 | 17.6 | 2.13 |
| 比較応用例 3 | 比較例 1 | 0.50 | 6.1 | — | — | 1.87 | 16.4 | 1.98 |
| 比較応用例 4 | 比較例 1 | 0.50 | 5.0 | — | — | 1.89 | 16.6 | 2.03 |

[0022]

[Table 3]

表. 3

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 17 | 実施例 1 | 0.25 | 5.0 | 5 | 200 | 1.70 | 14.7 | 1.73 |
| 応用例 18 | 実施例 1 | 0.25 | 5.0 | 10 | 200 | 1.68 | 14.7 | 1.74 |
| 応用例 19 | 実施例 2 | 0.25 | 5.0 | 5 | 200 | 1.76 | 15.1 | 1.76 |
| 応用例 20 | 実施例 2 | 0.25 | 5.0 | 10 | 200 | 1.75 | 14.9 | 1.76 |
| 応用例 21 | 実施例 3 | 0.25 | 5.0 | 5 | 200 | 1.80 | 15.6 | 1.88 |
| 応用例 22 | 実施例 3 | 0.25 | 5.0 | 10 | 200 | 1.77 | 15.4 | 1.86 |
| 応用例 23 | 実施例 4 | 0.25 | 5.0 | 5 | 200 | 1.79 | 15.6 | 1.89 |
| 応用例 24 | 実施例 4 | 0.25 | 5.0 | 10 | 200 | 1.79 | 15.6 | 1.86 |
| 比較応用例 5 | 比較例 1 | 0.25 | 5.0 | 5 | 200 | 1.70 | 14.7 | 1.74 |
| 比較応用例 6 | 比較例 1 | 0.25 | 5.0 | 10 | 200 | 1.69 | 14.6 | 1.72 |

[0023]

[Table 4]

表. 4

| 応用 | 添加剤 | 添加量 (%) | 抄紙 pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|-------|------------|-------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 2 5 | 実施例 1 | 0.50 | 5.0 | 5 | 200 | 1.86 | 16.3 | 1.97 |
| 応用例 2 6 | 実施例 1 | 0.50 | 5.0 | 10 | 200 | 1.85 | 16.0 | 1.96 |
| 応用例 2 7 | 実施例 2 | 0.50 | 5.0 | 5 | 200 | 1.89 | 16.3 | 2.00 |
| 応用例 2 8 | 実施例 2 | 0.50 | 5.0 | 10 | 200 | 1.88 | 16.3 | 1.98 |
| 応用例 2 9 | 実施例 3 | 0.50 | 5.0 | 5 | 200 | 1.98 | 17.1 | 2.06 |
| 応用例 3 0 | 実施例 3 | 0.50 | 5.0 | 10 | 200 | 1.95 | 16.8 | 2.02 |
| 応用例 3 1 | 実施例 4 | 0.50 | 5.0 | 5 | 200 | 1.99 | 17.1 | 2.06 |
| 応用例 3 2 | 実施例 4 | 0.50 | 5.0 | 10 | 200 | 1.97 | 17.0 | 2.03 |
| 比較応用例 7 | 比較例 1 | 0.50 | 5.0 | 5 | 200 | 1.85 | 16.2 | 1.96 |
| 比較応用例 8 | 比較例 1 | 0.50 | 5.0 | 10 | 200 | 1.84 | 16.0 | 1.95 |

[0024]

[Table 5]

表. 5

[0025]
[Table 6]

| 応用 | 添加剤 | 添加量 (%) | 抄紙 pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|-----------|-------|------------|-------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 3 3 | 実施例 5 | 0.25 | 6.1 | — | — | 1.74 | 15.5 | 1.75 |
| 応用例 3 4 | 実施例 5 | 0.25 | 5.0 | — | — | 1.78 | 15.9 | 1.77 |
| 応用例 3 5 | 実施例 6 | 0.25 | 6.1 | — | — | 1.77 | 15.8 | 1.79 |
| 応用例 3 6 | 実施例 6 | 0.25 | 5.0 | — | — | 1.76 | 15.9 | 1.82 |
| 応用例 3 7 | 実施例 7 | 0.25 | 6.1 | — | — | 1.82 | 16.0 | 1.89 |
| 応用例 3 8 | 実施例 7 | 0.25 | 5.0 | — | — | 1.83 | 15.9 | 1.88 |
| 応用例 3 9 | 実施例 8 | 0.25 | 6.1 | — | — | 1.85 | 16.2 | 1.90 |
| 応用例 4 0 | 実施例 8 | 0.25 | 5.0 | — | — | 1.81 | 15.8 | 1.87 |
| 比較応用例 9 | 比較例 2 | 0.25 | 6.1 | — | — | 1.72 | 15.3 | 1.71 |
| 比較応用例 1 0 | 比較例 2 | 0.25 | 5.0 | — | — | 1.75 | 15.8 | 1.74 |

表. 6

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|-----------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 4 1 | 実施例 5 | 0.50 | 6.1 | — | — | 1.88 | 16.1 | 1.93 |
| 応用例 4 2 | 実施例 5 | 0.50 | 5.0 | — | — | 1.92 | 16.6 | 1.91 |
| 応用例 4 3 | 実施例 6 | 0.50 | 6.1 | — | — | 1.92 | 16.6 | 1.93 |
| 応用例 4 4 | 実施例 6 | 0.50 | 5.0 | — | — | 1.95 | 15.9 | 1.97 |
| 応用例 4 5 | 実施例 7 | 0.50 | 6.1 | — | — | 2.01 | 16.8 | 1.99 |
| 応用例 4 6 | 実施例 7 | 0.50 | 5.0 | — | — | 2.00 | 17.0 | 2.08 |
| 応用例 4 7 | 実施例 8 | 0.50 | 6.1 | — | — | 2.01 | 17.6 | 2.13 |
| 応用例 4 8 | 実施例 8 | 0.50 | 5.0 | — | — | 1.98 | 17.1 | 2.05 |
| 比較応用例 1 1 | 比較例 2 | 0.50 | 6.1 | — | — | 1.86 | 15.9 | 1.90 |
| 比較応用例 1 2 | 比較例 2 | 0.50 | 5.0 | — | — | 1.89 | 16.6 | 2.03 |

[0026]

[Table 7]

表. 7

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例49 | 実施例5 | 0.25 | 5.0 | 5 | 200 | 1.86 | 14.5 | 1.76 |
| 応用例50 | 実施例5 | 0.25 | 5.0 | 10 | 200 | 1.65 | 14.4 | 1.74 |
| 応用例51 | 実施例6 | 0.25 | 5.0 | 5 | 200 | 1.69 | 14.7 | 1.76 |
| 応用例52 | 実施例6 | 0.25 | 5.0 | 10 | 200 | 1.67 | 14.6 | 1.75 |
| 応用例53 | 実施例7 | 0.25 | 5.0 | 5 | 200 | 1.73 | 14.8 | 1.81 |
| 応用例54 | 実施例7 | 0.25 | 5.0 | 10 | 200 | 1.72 | 14.7 | 1.77 |
| 応用例55 | 実施例8 | 0.25 | 5.0 | 5 | 200 | 1.73 | 14.9 | 1.79 |
| 応用例56 | 実施例8 | 0.25 | 5.0 | 10 | 200 | 1.71 | 14.7 | 1.78 |
| 比較応用例13 | 比較例2 | 0.25 | 5.0 | 5 | 200 | 1.65 | 14.7 | 1.76 |
| 比較応用例14 | 比較例2 | 0.25 | 5.0 | 10 | 200 | 1.63 | 14.4 | 1.73 |

[0027]

[Table 8]

表. 8

| 応用 | 添加剤 | 添加量 (%) | 抄紙 pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|-----------|-------|------------|-------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 5 7 | 実施例 5 | 0.50 | 5.0 | 5 | 200 | 1.82 | 15.6 | 1.85 |
| 応用例 5 8 | 実施例 5 | 0.50 | 5.0 | 10 | 200 | 1.80 | 15.4 | 1.84 |
| 応用例 5 9 | 実施例 6 | 0.50 | 5.0 | 5 | 200 | 1.85 | 15.8 | 1.89 |
| 応用例 6 0 | 実施例 6 | 0.50 | 5.0 | 10 | 200 | 1.86 | 15.7 | 1.87 |
| 応用例 6 1 | 実施例 7 | 0.50 | 5.0 | 5 | 200 | 1.92 | 16.0 | 1.96 |
| 応用例 6 2 | 実施例 7 | 0.50 | 5.0 | 10 | 200 | 1.88 | 16.0 | 1.93 |
| 応用例 6 3 | 実施例 8 | 0.50 | 5.0 | 5 | 200 | 1.93 | 16.1 | 1.94 |
| 応用例 6 4 | 実施例 8 | 0.50 | 5.0 | 10 | 200 | 1.90 | 16.0 | 1.94 |
| 比較応用例 1 5 | 比較例 2 | 0.50 | 5.0 | 5 | 200 | 1.80 | 15.6 | 1.85 |
| 比較応用例 1 6 | 比較例 2 | 0.50 | 5.0 | 10 | 200 | 1.79 | 15.3 | 1.83 |

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the manufacture approach of the paper reinforcing agent of paper. Furthermore, in detail, to fluctuation of pH (paper making pH is called hereafter) of the pulp slurry at the time of carrying out paper making of the copolymer manufactured with the polymerization method of this invention, fluctuation of effectiveness is small and the fall of effectiveness offers the approach that a small paper reinforcing agent can be manufactured, to the mineral salt of the dissolution component which exists in a pulp slurry, for example, a sodium sulfate, a calcium sulfate, etc.

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PRIOR ART

[Description of the Prior Art] The former and a paper reinforcing agent have independent use of anionic polyacrylamide (polyacrylamide is hereafter called Pulse Amplitude Modulation) in use. ***** Further improvement in the shift to closed ** or neutral paper making of Hokusui by problems, such as wastewater regulation, poor fixing of the sizing compound accompanying it, filterability, a loading material yield, etc. is made into the purpose. According to concomitant use of anionic Pulse Amplitude Modulation and both sexes (cation) Pulse Amplitude Modulation Filterability ability, the fixing engine performance of a loading material or a sizing compound, the paper durability effectiveness, etc. have improved. Moreover, recently, the simultaneous adding formula of anionic Pulse Amplitude Modulation and both sexes (cation) Pulse Amplitude Modulation and a mixed addition formula are developed, and fixing of the further filterability ability and a sizing compound and the paper durability effectiveness can be expected now. However, in respect of a facility, it is [2 sequence] necessary for the object for anions, and for both sexes (cation). Moreover, it is known that the whiteness degree to which importance is attached in the western paper field will also fall greatly. up to the microfilament to which this reduces a whiteness degree greatly by condensation of anionic Pulse Amplitude Modulation and both sexes (cation) Pulse Amplitude Modulation, the dust in the Hokusui system, etc. -- Kaminaka -- yield **** -- things are a big factor. Furthermore, also when the fall of the formation of paper poses a problem from the strength of cohesive force, it has come out. Recently comes and the paper reinforcing agent manufactured considering the cationic vinyl system monomer and acrylamide of the quarternary ammonium salt obtained by the reaction with the vinyl system monomers which have the 3rd class amino group, those salts, and/or the 4th class-sized agent as a main raw material is beginning to be used considerably. Generally these paper reinforcing agents are used independently, and have an effective paper-making pH field comparatively large as independent use, and paper durability reinforcement, the fixing effectiveness of a sizing compound, the yield effectiveness of a loading material, the description that a whiteness degree fall is small, etc. are acquired. however, compared with the conventional anion Pulse Amplitude Modulation and concomitant use of both sexes (cation) Pulse Amplitude Modulation, it is now in respect of the reinforcement in these independent use -- what is satisfied is not obtained.

[Translation done.]

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- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] the both-sexes polymer of the former [polymer / which was manufactured the condition in this invention generic claim as shown in Tables 1-8 / both-sexes] -- a ratio -- bursting strength and a ratio -- it excels in engine performance, such as an improvement operation in paper durability shown by compressive strength and Z-axis reinforcement, and is hard to be influenced by pH fluctuation.

[0020]

[Table 1]

表. 1

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 1 | 実施例 1 | 0.25 | 6.1 | — | — | 1.76 | 15.8 | 1.77 |
| 応用例 2 | 実施例 1 | 0.25 | 5.0 | — | — | 1.77 | 15.8 | 1.80 |
| 応用例 3 | 実施例 2 | 0.25 | 6.1 | — | — | 1.77 | 15.9 | 1.81 |
| 応用例 4 | 実施例 2 | 0.25 | 5.0 | — | — | 1.79 | 15.8 | 1.85 |
| 応用例 5 | 実施例 3 | 0.25 | 6.1 | — | — | 1.85 | 16.1 | 1.91 |
| 応用例 6 | 実施例 3 | 0.25 | 5.0 | — | — | 1.84 | 15.9 | 1.93 |
| 応用例 7 | 実施例 4 | 0.25 | 6.1 | — | — | 1.86 | 16.2 | 1.93 |
| 応用例 8 | 実施例 4 | 0.25 | 5.0 | — | — | 1.84 | 16.0 | 1.92 |
| 比較応用例 1 | 比較例 1 | 0.25 | 6.1 | — | — | 1.74 | 15.7 | 1.81 |
| 比較応用例 2 | 比較例 1 | 0.25 | 5.0 | — | — | 1.75 | 15.8 | 1.82 |

[0021]
[Table 2]

表. 2

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 9 | 実施例 1 | 0.50 | 6.1 | — | — | 1.90 | 16.4 | 1.99 |
| 応用例 10 | 実施例 1 | 0.50 | 5.0 | — | — | 1.91 | 16.9 | 2.03 |
| 応用例 11 | 実施例 2 | 0.50 | 6.1 | — | — | 1.91 | 16.8 | 2.03 |
| 応用例 12 | 実施例 2 | 0.50 | 5.0 | — | — | 1.93 | 16.9 | 2.05 |
| 応用例 13 | 実施例 3 | 0.50 | 6.1 | — | — | 2.02 | 17.7 | 2.09 |
| 応用例 14 | 実施例 3 | 0.50 | 5.0 | — | — | 2.00 | 17.6 | 2.09 |
| 応用例 15 | 実施例 4 | 0.50 | 6.1 | — | — | 2.03 | 17.8 | 2.11 |
| 応用例 16 | 実施例 4 | 0.50 | 5.0 | — | — | 2.02 | 17.6 | 2.13 |
| 比較応用例 3 | 比較例 1 | 0.50 | 6.1 | — | — | 1.87 | 16.4 | 1.98 |
| 比較応用例 4 | 比較例 1 | 0.50 | 5.0 | — | — | 1.89 | 16.6 | 2.03 |

[0022]

[Table 3]

表. 3

| 応用 | 添加剤 | 添加量 (%) | 抄紙 pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z 軸強度 (Kg/cm) |
|---------|-------|------------|-------|----------------------------------------|----------------------------|-------|-------|------------------|
| 応用例 17 | 実施例 1 | 0.25 | 5.0 | 5 | 200 | 1.70 | 14.7 | 1.73 |
| 応用例 18 | 実施例 1 | 0.25 | 5.0 | 10 | 200 | 1.68 | 14.7 | 1.74 |
| 応用例 19 | 実施例 2 | 0.25 | 5.0 | 5 | 200 | 1.76 | 15.1 | 1.76 |
| 応用例 20 | 実施例 2 | 0.25 | 5.0 | 10 | 200 | 1.75 | 14.9 | 1.76 |
| 応用例 21 | 実施例 3 | 0.25 | 5.0 | 5 | 200 | 1.80 | 15.6 | 1.88 |
| 応用例 22 | 実施例 3 | 0.25 | 5.0 | 10 | 200 | 1.77 | 15.4 | 1.86 |
| 応用例 23 | 実施例 4 | 0.25 | 5.0 | 5 | 200 | 1.79 | 15.6 | 1.89 |
| 応用例 24 | 実施例 4 | 0.25 | 5.0 | 10 | 200 | 1.79 | 15.6 | 1.86 |
| 比較応用例 5 | 比較例 1 | 0.25 | 5.0 | 5 | 200 | 1.70 | 14.7 | 1.74 |
| 比較応用例 6 | 比較例 1 | 0.25 | 5.0 | 10 | 200 | 1.69 | 14.6 | 1.72 |

[0023]

[Table 4]

表. 4

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|--------|------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例25 | 実施例1 | 0.50 | 5.0 | 5 | 200 | 1.86 | 16.3 | 1.97 |
| 応用例26 | 実施例1 | 0.50 | 5.0 | 10 | 200 | 1.85 | 16.0 | 1.96 |
| 応用例27 | 実施例2 | 0.50 | 5.0 | 5 | 200 | 1.89 | 16.3 | 2.00 |
| 応用例28 | 実施例2 | 0.50 | 5.0 | 10 | 200 | 1.88 | 16.3 | 1.98 |
| 応用例29 | 実施例3 | 0.50 | 5.0 | 5 | 200 | 1.98 | 17.1 | 2.06 |
| 応用例30 | 実施例3 | 0.50 | 5.0 | 10 | 200 | 1.95 | 16.8 | 2.02 |
| 応用例31 | 実施例4 | 0.50 | 5.0 | 5 | 200 | 1.99 | 17.1 | 2.06 |
| 応用例32 | 実施例4 | 0.50 | 5.0 | 10 | 200 | 1.97 | 17.0 | 2.03 |
| 比較応用例7 | 比較例1 | 0.50 | 5.0 | 5 | 200 | 1.85 | 16.2 | 1.96 |
| 比較応用例8 | 比較例1 | 0.50 | 5.0 | 10 | 200 | 1.84 | 16.0 | 1.95 |

[0024]

[Table 5]

表. 5

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例33 | 実施例5 | 0.25 | 6.1 | — | — | 1.74 | 15.5 | 1.75 |
| 応用例34 | 実施例5 | 0.25 | 5.0 | — | — | 1.78 | 15.9 | 1.77 |
| 応用例35 | 実施例6 | 0.25 | 6.1 | — | — | 1.77 | 15.8 | 1.79 |
| 応用例36 | 実施例6 | 0.25 | 5.0 | — | — | 1.76 | 15.9 | 1.82 |
| 応用例37 | 実施例7 | 0.25 | 6.1 | — | — | 1.82 | 16.0 | 1.89 |
| 応用例38 | 実施例7 | 0.25 | 5.0 | — | — | 1.83 | 15.9 | 1.88 |
| 応用例39 | 実施例8 | 0.25 | 6.1 | — | — | 1.85 | 16.2 | 1.90 |
| 応用例40 | 実施例8 | 0.25 | 5.0 | — | — | 1.81 | 15.8 | 1.87 |
| 比較応用例9 | 比較例2 | 0.25 | 6.1 | — | — | 1.72 | 15.3 | 1.71 |
| 比較応用例10 | 比較例2 | 0.25 | 5.0 | — | — | 1.75 | 15.8 | 1.74 |

[0025]

[Table 6]

表. 6

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|-----------|-------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 4 1 | 実施例 5 | 0.50 | 6.1 | — | — | 1.88 | 16.1 | 1.93 |
| 応用例 4 2 | 実施例 5 | 0.50 | 5.0 | — | — | 1.92 | 16.6 | 1.91 |
| 応用例 4 3 | 実施例 6 | 0.50 | 6.1 | — | — | 1.92 | 16.6 | 1.93 |
| 応用例 4 4 | 実施例 6 | 0.50 | 5.0 | — | — | 1.95 | 15.9 | 1.97 |
| 応用例 4 5 | 実施例 7 | 0.50 | 6.1 | — | — | 2.01 | 16.8 | 1.99 |
| 応用例 4 6 | 実施例 7 | 0.50 | 5.0 | — | — | 2.00 | 17.0 | 2.08 |
| 応用例 4 7 | 実施例 8 | 0.50 | 6.1 | — | — | 2.01 | 17.6 | 2.13 |
| 応用例 4 8 | 実施例 8 | 0.50 | 5.0 | — | — | 1.98 | 17.1 | 2.05 |
| 比較応用例 1 1 | 比較例 2 | 0.50 | 6.1 | — | — | 1.86 | 15.9 | 1.90 |
| 比較応用例 1 2 | 比較例 2 | 0.50 | 5.0 | — | — | 1.89 | 16.8 | 2.03 |

[0026]

[Table 7]

表. 7

| 応用 | 添加剤 | 添加量 (%) | 抄紙pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|---------|------|------------|------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例49 | 実施例5 | 0.25 | 5.0 | 5 | 200 | 1.66 | 14.5 | 1.76 |
| 応用例50 | 実施例5 | 0.25 | 5.0 | 10 | 200 | 1.65 | 14.4 | 1.74 |
| 応用例51 | 実施例6 | 0.25 | 5.0 | 5 | 200 | 1.69 | 14.7 | 1.76 |
| 応用例52 | 実施例6 | 0.25 | 5.0 | 10 | 200 | 1.67 | 14.6 | 1.75 |
| 応用例53 | 実施例7 | 0.25 | 5.0 | 5 | 200 | 1.73 | 14.8 | 1.81 |
| 応用例54 | 実施例7 | 0.25 | 5.0 | 10 | 200 | 1.72 | 14.7 | 1.77 |
| 応用例55 | 実施例8 | 0.25 | 5.0 | 5 | 200 | 1.73 | 14.9 | 1.79 |
| 応用例56 | 実施例8 | 0.25 | 5.0 | 10 | 200 | 1.71 | 14.7 | 1.78 |
| 比較応用例13 | 比較例2 | 0.25 | 5.0 | 5 | 200 | 1.65 | 14.7 | 1.76 |
| 比較応用例14 | 比較例2 | 0.25 | 5.0 | 10 | 200 | 1.63 | 14.4 | 1.73 |

[0027]

[Table 8]

表. 8

| 応用 | 添加剤 | 添加量 (%) | 抄紙 pH | Na ₂ SO ₄ (%) | CaSO ₄ (ppm) | 比破裂強度 | 比圧縮強度 | Z軸強度 (Kg/cm) |
|-----------|-------|------------|-------|----------------------------------------|----------------------------|-------|-------|-----------------|
| 応用例 5 7 | 実施例 5 | 0.50 | 5.0 | 5 | 200 | 1.82 | 15.6 | 1.85 |
| 応用例 5 8 | 実施例 5 | 0.50 | 5.0 | 10 | 200 | 1.80 | 15.4 | 1.84 |
| 応用例 5 9 | 実施例 6 | 0.50 | 5.0 | 5 | 200 | 1.85 | 15.8 | 1.89 |
| 応用例 6 0 | 実施例 6 | 0.50 | 5.0 | 10 | 200 | 1.86 | 15.7 | 1.87 |
| 応用例 6 1 | 実施例 7 | 0.50 | 5.0 | 5 | 200 | 1.92 | 16.0 | 1.96 |
| 応用例 6 2 | 実施例 7 | 0.50 | 5.0 | 10 | 200 | 1.88 | 16.0 | 1.93 |
| 応用例 6 3 | 実施例 8 | 0.50 | 5.0 | 5 | 200 | 1.93 | 16.1 | 1.94 |
| 応用例 6 4 | 実施例 8 | 0.50 | 5.0 | 10 | 200 | 1.90 | 16.0 | 1.94 |
| 比較応用例 1 5 | 比較例 2 | 0.50 | 5.0 | 5 | 200 | 1.80 | 15.6 | 1.85 |
| 比較応用例 1 6 | 比較例 2 | 0.50 | 5.0 | 10 | 200 | 1.79 | 15.3 | 1.83 |

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention by changing the manufacture approach of the paper reinforcing agent manufactured considering the cationic vinyl system monomer and acrylamide of the quarternary ammonium salt obtained by the reaction with the vinyl system monomers which have the conventional 3rd class amino group, those salts, and/or the 4th class-ized agent as a main raw material The paper durability effectiveness is high, and fluctuation of effectiveness is [as opposed to / further / fluctuation of pH] small, and fluctuation of effectiveness offers a small paper reinforcing agent to the dissolution component which exists in a pulp slurry.

[Translation done.]

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MEANS

[Means for Solving the Problem] The quarternary ammonium salt (a) obtained by the reaction with the vinyl system monomers which have the 3rd class amino group, those salts, and/or the 4th class-sized agent this invention Namely, 0.5 - 20-mol%, The vinyl system monomers which have a carboxyl group and/or a sulfone radical, and those salts (b) 0.5 - 20-mol%, Polyvinyl system monomer (c) 0.01-2 mol%, acrylamide (meta) (d) It is related with the manufacture approach of the paper reinforcing agent characterized by carrying out the polymerization of the configuration monomer component which consists of 55 - 98.99mol% by the following approach. The manufacture approach of the paper reinforcing agent considered as a polymerization and the mark by carrying out continuation dropping of [1 (a)], (b), (c), and the (d). By carrying out continuation dropping of (a), (b), and the (d) under [2] (c) existence, a polymerization, It is a polymerization and [0005] by carrying out continuation dropping of (a) and the (d), after carrying out a polymerization by carrying out continuation dropping of (b) and the (d) under a polymerization and existence of [4 (c)] by carrying out continuation dropping of (a) and the (d) after carrying out the polymerization of [3 (b)], (c), and the (d). The quarternary ammonium salt hereafter obtained in this invention which explains this invention to a detail by the reaction of the vinyl system monomer and the 4th class-sized agent which have the 3rd class amino group is for example, dimethylaminopropyl (meta) acrylate, dimethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylamide, diethylamino propyl (meta) acrylamide, etc. With the 4th class-sized agent in this invention, chloromethane, benzyl chloride, a p-chlorobenzyl chloride, p-methylbenzyl chloride, p-nitrobenzyl chloride, etc. are lifted. The vinyl system monomer which has quarternary ammonium salt by the reaction of the vinyl system monomer and the 4th class-sized agent which have this the 3rd class amino group can be offered. These amounts of monomers used are usually 0.5-20-mol%, and are 1-10-mol% preferably. 0. Less than [5mol%], a polymer is hard to be fixed to pulp fiber, and there is un-arranging [that the paper durability effectiveness cannot fully be discovered]. It becomes a loss economically and is inconvenient if 20-mol% is exceeded. The vinyl system monomers which have the carboxyl group used for this invention, and those salts can illustrate unsaturated carboxylic acid and those salts, such as a maleic acid, a fumaric acid, an itaconic acid, an acrylic acid (meta), a crotonic acid, or a citraconic acid. The vinyl system monomers which have a sulfone radical, and those salts can illustrate partial saturation sulfonic acids and those salts, such as a vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound (meta) sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, and a 2-acrylamide-2-phenyl propane sulfonic acid. These amounts of monomers used are usually 0.5-20-mol%, and are 1-10-mol% preferably. 0. Less than [5mol%], if there is un-arranging on the problem on fixing to the pulp of a paper durability agent and 20-mol% is exceeded, the balance of the amount of cations in a paper durability agent and the amount of anions will pose a problem, and there is un-arranging [that the paper durability effectiveness cannot fully be discovered].

[0006] With the polyvinyl system monomer of this invention, the monomer which has at least two or more double bonds can be raised into a molecule. Specifically, methylenebis acrylamide, diaryl acrylamide, triacrylformal, diacryloyl imide, ethylene glycol acrylate, ethylene glycol dimethacrylate, propylene glycol diacrylate, 1, 3-butylene-glycol dimethacrylate, 1, 4-butylene-

glycol dimethacrylate, glycerol dimethacrylate neopentyl glycol dimethacrylate, trimethylolpropane triacrylate, a divinylbenzene, diallyl phthalate, etc. can be used. Although these amounts used change with classes of polyvinyl system monomer and do not generally have *****, it is usually 0.01-2-mol%, and is 0.01-1-mol% preferably. 0. Less than [0.01mol%], when there is un-arranging [that the paper durability effectiveness cannot fully be discovered] and two-mol% is exceeded, there is un-arranging [that gelation takes place]. If the acrylamide used by this invention (meta) is marketed in the state of fine particles or a water solution and is used industrially, it is enough.

[0007] If it is furthermore a water-soluble object as a polymerization initiator, there will be especially no limit and it will usually be used, dissolving in a monomer water solution. Specifically, the superphosphate like the bromate like a hydrogen peroxide, the peroxide like a benzoyl peroxide, sodium persulfate, potassium persulfate, the persulfate like ammonium persulfate, sodium bromate, and a potassium bromate, fault boron acid sodium, a fault boron acid potassium, fault boron acid ammonium ***** boron acid chloride, a fault sodium carbonate, potassium percarbonate, fault ammonium-carbonate **** percarbonate, perphosphoric acid sodium, a perphosphoric acid potassium, and perphosphoric acid ammonium etc. is mentioned. In this case, although it can be used even if independent, it can use also as a redox system polymerization agent combining a reducing agent. a reducing agent -- ***** -- for example -- a sulfite -- a hydrogensulfite -- iron -- copper -- cobalt -- etc. -- low -- a degree -- ionization -- a salt -- N -- N -- N -- ' -- N -- ' -- tetramethylethylenediamine -- etc. -- organic -- an amine -- reducing sugars, such as ADOSU and a ketose, etc. can be mentioned further. Moreover, as an azo compound, a - azobis-2,4-dimethylvaleronitrile, and 2 and 2'-azobis-4-amidinopropane hydrochloride, 2, and 2' 4, 4'-azobis-4-cyano BAREIN acid, its salt, etc. can be used.

Furthermore, it is also possible to use together two or more sorts of above-mentioned polymerization initiators. Polymerization temperature is 30-90 degrees C in general, and it is desirable to control generation of heat by the polymerization and to make the temperature change small. Moreover, it is better for inert gas like nitrogen gas to permute with making a polymerization perform promptly, although especially limitation does not have an ambient atmosphere in curing units. Although especially limitation does not have the continuation drop time of a monomer, it is 40 - 120 minutes preferably in general at 40 - 180 minutes. There are 2 - 4 hours of polymerization time amount preferably in general in 2 - 20 hours.

[0008] The paper reinforcing agent manufactured by the approach of this invention is used in the process which carries out paper making of the pulp, and brings about a big effect for reinforcing the filtration improvement for improving the water break at the time of paper making, and the mechanical reinforcement of paper etc. Although the paper reinforcing agent manufactured by the approach of this invention can also be independently used at this time, you may use together with a sulfuric-acid band, anionic polyacrylamide, MANNIHHI denaturation polyacrylamide, the Hoffmann denaturation polyacrylamide, etc. The addition of the paper reinforcing agent of this invention is each to the desiccation solid content weight of pulp, although it changes with the class of pulp, the speed of paper making, etc. and there is no ***** generally. It is 0.05 - 1% of range preferably 0.01 to 3%. If an addition location is before forming a humid sheet, it will be good anywhere and will usually be added from a refiner outlet before an inlet. In the paper-making system in which a lot of salts exist, the paper durability effectiveness is demonstrated in broad pH field, and the paper manufactured by the above approaches is specifically excellent in bursting strength, compressive strength, Z-axis reinforcement, etc. Therefore, it becomes possible by applying this invention to manufacture paper with the outstanding paper durability reinforcement. The polymer which constructed the bridge partially when the polymerization was carried out about this reason using a polyvinyl monomer like the divinyl monomer of a small amount or a TORIBI nil monomer, although it was not certain generates, and if a monomer is supplied continuously and carries out a polymerization to this, it will become that a polymerization is easy to be carried out by this polymer that constructed the bridge. Therefore, since a polymer has a particle-motion highly [molecular weight], it is thought that it has become that it cannot be easily influenced by pH or ionic strength of a pulp slurry at the time of this paper reinforcing agent being established to pulp.

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EXAMPLE

[Example] Next, although this invention is divided into the example of manufacture, and an application according to an example and is explained concretely, this invention is not necessarily limited to the following examples. Moreover, it has set by the GPC method (ShodexGPC System-11, column KB-80M use), and it is 0.1N-NaNO₃ that it is with weight average molecular weight. Water solution: It is the thing of the polyethylene-glycol reduced property in formamide =3:7 mixed-liquor lower.

To an example 1 Griffin beaker, 312.72 g (91.94-mol%) 40% acrylamide, 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride, 80% 1.72 g (one-mol%) acrylic-acid and itaconic-acid 7.47g (three-mol%) methylenebis acrylamide 177mg (0.06mol%) is adjusted to pH 4.5 in ammoniacal liquor brewing **28%, It considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted 558.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Blowing nitrogen gas after an appropriate time, it agitated and the temperature up of the internal temperature was carried out to 50 degrees C with the water bath. (A) While starting continuation dropping of a solution, continuation dropping of 50g of ammonium persulfate water solutions and the 50g of the sodium-hydrogensulfite water solutions was carried out, the polymerization was started, and the (A) solution was dropped over 70 minutes. Nonvolatile matter 15.7%, Brookfield viscosity in 25 degrees C when it was fixed 50 degrees C and was made to react for 3 hours The both-sexes polymer water solution of the isoelectric point pH 4.8 in 9, 290 cps, pH4.1, weight average molecular weight 800,000, and turbidity was obtained.

[0010] 312.72 g (91.94-mol%) 40% acrylamide, 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride, 1.72 g (one-mol%) 80% acrylic acid, and the 7.47 g (three-mol%) itaconic acid were adjusted to pH 4.5 in ammoniacal liquor brewing **28% at the example 2 Griffin beaker, and it considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 177mg (0.06mol%) and 558.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 4.8 in 15.5% of nonvolatile matters, the Brookfield viscosity 8 in 25 degrees C, 150 cps, pH4.0, weight average molecular weight 1 million, and turbidity.

The brewing **2.5% sulfuric acid adjusted 40% acrylamide 293.17g (86.19mol%) and 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride to pH 4.5 at the example 3 Griffin beaker, and it considered as the (A) solution. In 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 19.55 g (5.75mol%) 40% acrylamide, 1.72 g (one-mol%) acrylic-acid, 7.47 g (three-mol%) itaconic-acid, and methylenebis acrylamide 177mg (0.06mol%) and 558.06 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 80%. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 5.5 in nonvolatile matter 15.7%, the Brookfield viscosity 8 in 25 degrees C, 730 cps, pH4.7, weight average molecular weight 1,300,000, and turbidity.

[0011] 19.55 g (5.75-mol%) acrylamide, 1.72 g (one-mol%) 80% acrylic acid, 7.47g (three-mol%) of

itaconic acids, and 58.63 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 40% at the example 4 Griffin beaker, and it considered as the (A) solution. Moreover, the brewing **2.5% sulfuric acid adjusted 40% acrylamide 293.17g (86.19mol%) and 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride to pH 4.5 at the Griffin beaker, and it considered as the (B) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 177mg (0.06mol%) and 499.43 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Blowing nitrogen gas after an appropriate time, it agitated and the temperature up of the internal temperature was carried out to 50 degrees C with the water bath. (A) While starting continuation dropping of a solution, continuation dropping of 50g of ammonium persulfate water solutions and the 50g of the sodium-hydrogensulfite water solutions was carried out, and the polymerization was started. (A) The solution was dropped over 14 minutes, it set for 10 minutes and the (B) solution was dropped over 56 minutes. It was fixed 50 degrees C, and when it was made to react for 3 hours, the both-sexes polymer water solution of the isoelectric point pH 5.5 in nonvolatile matter 15.7%, the Brookfield viscosity 9 in 25 degrees C, 600 cps, pH4.7, weight average molecular weight 1,300,000, and turbidity was obtained.

[0012] In 4 opening flask equipped with example of comparison 1 agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 312.72 g (91.94mol%) 40% acrylamide, 19.86 g (four-mol%) 80%N-methacryloiloxy-ethyl trimethylammonium chloride, It brewing ** Ranked second and caustic alkali of sodium adjusted 80% 1.72 g (one-mol%) acrylic-acid, 7.47 g (three-mol%) itaconic-acid, and methylenebis acrylamide 177mg (0.06mol%) and 625.79 g water to pH 4.2 20%. The internal temperature was covered with the back heat insulating material which carried out the temperature up to 50 degrees C, blowing nitrogen gas after an appropriate time. Agitating, the ammonium persulfate water solution and 10% sodium-hydrogensulfite water solution were thrown in 10%, and the polymerization was started. When water was thrown in after [of reaction peak attainment] 10 minutes and the polymerization reaction was made to complete, the both-sexes polymer water solution of the isoelectric point pH 4.8 in nonvolatile matter 15.4%, the Brookfield viscosity 7 in 25 degrees C, 850 cps, pH4.3, weight average molecular weight 500,000, and turbidity was obtained.

It is 40% acrylamide to an example 5 Griffin beaker. A sulfuric acid adjusts 320.99 g (91.94mol%), 12.34 g (four-mol%) dimethylaminoethyl methacrylate, and 77 g (one-mol%) and 7.67g (three-mol%) methylenebis acrylamide [of 80% acrylic-acid 1. itaconic acids] 182mg (0.06mol%) to pH 4.5 brewing **20%, It considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted 539.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 4.3 in nonvolatile matter 15.6%, the Brookfield viscosity 8 in 25 degrees C, 430 cps, pH4.1, weight average molecular weight 700,000, and turbidity.

[0013] The sulfuric acid adjusted 320.99 g (91.94-mol%) acrylamide, 12.34 g (four-mol%) dimethylaminoethyl methacrylate, 1.77 g (one-mol%) 80% acrylic acid, and the 7.67 g (three-mol%) itaconic acid to pH 4.5 brewing **20% 40% at the example 6 Griffin beaker, and it considered as the (A) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 182mg (0.06mol%) and 539.06 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 1, and obtained the both-sexes polymer water solution of the isoelectric point pH 4.3 in nonvolatile matter 15.5%, the Brookfield viscosity 10 in 25 degrees C, 260 cps, pH 4.1 weight average molecular weight 1 million, and turbidity.

The sulfuric acid adjusted 300.93 g (86.19-mol%) acrylamide and 12.34 g (four-mol%) dimethylaminoethyl methacrylate to pH 4.5 brewing **20% 40% at the example 7 Griffin beaker, and it considered as the (A) solution. In 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 20.06 g (5.75mol%) 40% acrylamide, 1.77 g (one-mol%) acrylic-acid, 7.67 g (three-mol%) itaconic-acid, and methylenebis acrylamide 182mg (0.06mol%) and 539.06 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 80%. Others performed the same actuation as an example 1, and obtained

the both-sexes polymer water solution of the isoelectric point pH 5.5 in nonvolatile matter 15.6%, the Brookfield viscosity 8 in 25 degrees C, 440 cps, pH4.7, weight average molecular weight 1,200,000, and turbidity.

[0014] 20.06 g (5.75-mol%) acrylamide, 1.77 g (one-mol%) 80% acrylic acid, 7.67 g (three-mol%) of itaconic acids, and 60.18 g water were adjusted to pH 4.5 in ammoniacal liquor after [the brewing ** dissolution] 28% 40% at the example 8 Griffin beaker, and it considered as the (A) solution. Moreover, it is 40% acrylamide 300.93g (86.19mol%) to the Griffin beaker. It is a brewing **20% sulfuric acid about dimethylaminoethyl methacrylate 12.34g (four-mol%). It adjusted to pH 4.5, and considered as the (B) solution. The brewing **2.5% sulfuric acid adjusted methylenebis acrylamide 182mg (0.06mol%) and 478.88 g water in 4 opening flask equipped with an agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing at pH 4.5. Others performed the same actuation as an example 4, and obtained the both-sexes polymer water solution of the isoelectric point pH 5.8 in nonvolatile matter 15.6%, the Brookfield viscosity 7 in 25 degrees C, 320 cps, pH4.8, weight average molecular weight 1,300,000, and turbidity.

[0015] In 4 opening flask equipped with example of comparison 2 agitator, a reflux cooling pipe, a thermometer, and nitrogen gas installation tubing, 320.99 g (91.94mol%) 40% acrylamide, 12.34 g (four-mol%) dimethylaminoethyl methacrylate, 80% 1.77 g (one-mol%) acrylic-acid, 7.67 g (three-mol%) itaconic-acid, and methylenebis acrylamide 182mg (0.06mol%) And it brewing ** Ranked second and the sulfuric acid adjusted 606.80 g water to pH 4.2 20%. Others performed the same actuation as the example 1 of a comparison, and obtained nonvolatile matter 15.6%, the Brookfield viscosity 6 in 25 degrees C, 970 cps, and the both-sexes polymer water solution of pH4.3.

concentration 1.0% which is 400ml (it is described as Canadian standard freeness and following C.S.F) of degrees of beating obtained from applications 1-8 and the comparison application 1 - 2 corrugated-paper used paper of pulp slurry -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. pH of the pulp slurry at this time was 6.1 and 5.0, respectively. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, and churning was continued for 1 more minute. The pulp slurry obtained after an appropriate time is used, and it is TAPPI. Paper making was carried out by the square shape sheet machine. With the drum dryer, for 110 degrees C and 3 minutes, the wet sheet which carried out paper making performed desiccation, and obtained the handmade paper of basis-weight 150 g/m2. the above handmade paper -- using -- JIS-P -8112 -- applying correspondingly -- a "burst index" and JIS-P -8126 -- applying correspondingly -- " -- a ratio -- "Z-axis reinforcement" was measured and computed using compressive-strength" and a Kumagaya Riki Kogyo internal bond tester, and the result was shown in Table 1.

[0016] applications 9-16 and the comparison applications 3-4 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 9-16 and the comparison applications 3-4 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 2.

applications 17-24 and the comparison applications 5-6 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na2 SO4 opposite pulp -- 5 or 10% -- adding -- CaSO4 opposite pulp -- 200 ppm It added and agitated for 2 minutes. Na2 SO4 adding -- the electric electric conductivity of a pulp slurry -- 0.15 mS/cm from -- 0.8 mS/cm and 1.3 second/cm It changed. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 17-24 and the comparison applications 5-6 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was

shown in Table 3.

[0017] applications 25-32 and the comparison applications 7-8 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na₂ SO₄ opposite pulp -- 5 or 10% -- adding -- CaSO₄ opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 1-4 and the example 1 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 25-32 and the comparison applications 7-8 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 4. applications 33-40 and the comparison applications 9-10 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 33-40 and the comparison applications 9-10 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 5.

applications 41-48 and the comparison applications 11-12 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- an aluminum sulfate -- dry weight criteria -- opposite pulp 0.5 -- 1.0% addition was carried out and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 41-48 and the comparison applications 11-12 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 6.

[0018] applications 49-56 and the comparison applications 13-14 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na₂ SO₄ opposite pulp -- 5 or 10% -- adding -- CaSO₄ opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.25% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 49-56 and the comparison applications 13-14 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 7. applications 57-64 and the comparison applications 15-16 -- the pulp slurry used in said applications 1-8 and the comparison applications 1-2 -- receiving -- Na₂ SO₄ opposite pulp -- 5 or 10% -- adding -- CaSO₄ opposite pulp -- 200 ppm It added and agitated for 2 minutes. 1for pulp.0% addition of the aluminum sulfate was carried out on dry weight criteria at it, and it agitated for 1 minute. Subsequently, 0.5% addition of the both-sexes polymer obtained in examples 5-8 and the example 2 of a comparison was carried out on dry weight criteria, measurement calculation of the physical properties of applications 57-64 and the comparison applications 15-16 was completely carried out in the same conditions and identity operation with applications 1-8 and the comparison applications 1-2, and the result was shown in Table 8.

[Translation done.]